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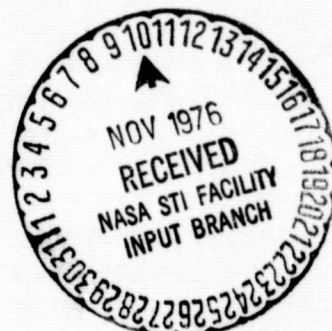
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HOT CORROSION STUDIES OF FOUR NICKEL-BASE SUPERALLOYS:

B-1900, NASA-TRW VIA, 713C and IN738

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ABSTRACT

The susceptibility to hot corrosion of four nickel-base superalloys has been studied at 900° and 1000°C in one atmosphere of slowly flowing oxygen. Hot corrosion was induced by coating the samples with known doses of Na_2SO_4 and oxidizing the coated samples isothermally on a sensitive microbalance. In general, the order of susceptibility found was: B-1900 > 713C > NASA-TRW VIA and > IN738. This order corresponds to the order of decreasing molybdenum content of the alloys. Chemical evidence for B-1900 indicates that hot corrosion is instigated by acid fluxing of the protective Al_2O_3 coating by MoO_3 .

INTRODUCTION

The continually increasing performance demanded from gas turbine engines requires ever increasing operating temperatures, which in turn, requires alloys with increased high temperature strength and corrosion resistance. Higher strength has been achieved in the nickel-base alloys used in turbine engines by increasing the amount of γ -forming elements, aluminum and titanium. This trend has provided alloys with good oxidation resistance but with decreased resistance to hot corrosion.

Most nickel-base superalloys are susceptible to hot corrosion attack to some extent. The hot corrosion phenomenon is known to be very complex, depending on many factors: temperature, composition of alloy, cyclic conditions, impurities in and pressure of air ingested into engine, and impurities in the fuel burned by the engine. Because of the complexity of the problem, research has been concerned mainly with phenomenological testing of alloys. Research directed toward an understanding of the reaction

mechanisms has been less prevalent, and as a result, a complete fundamental characterization of hot-corrosion is still lacking. An exception to this trend has been the work of Goebel, Pettit, and Goward (Ref. 1) and of Bornstein, DeCrescente, and Roth (Ref. 2).

As part of a larger program aimed at understanding the chemical mechanisms involved in hot corrosion, we have conducted a laboratory-test study involving isothermal, thermogravimetric rate determinations of the hot corrosion of four superalloys: NASA-TRW VIA, B-1900, Alloy 713C, and IN-738. Hot corrosion was induced by coating the samples with measured doses of Na_2SO_4 . Tests were conducted at 900° and 1000° C in one atmosphere of slowly flowing oxygen. As a basis for comparison, we have also determined the corrosion rates in simple oxidation.

Hot corrosion of superalloys usually displays an induction period before enhanced or catastrophic oxidation begins. This is a period of little or no weight gain; in this paper, less than 0.3 mg cm^{-2} . The length of the induction period is a function of the temperature, the composition of the alloy, the concentration of Na_2SO_4 , and the preoxidation treatment of the sample. We have been investigating the processes operative during and just after the induction period for samples of the four alloys that were preoxidized for 100 hours. The results obtained for B-1900 at 900° C with a coating of 3 mg cm^{-2} Na_2SO_4 are discussed in terms of the "acidic fluxing" mechanism of hot corrosion (Ref. 1).

EXPERIMENTAL

The alloy samples were obtained from commercial sources and were given conventional heat treatments.

The samples were $0.2 \times 1.0 \times 2.5 \text{ cm}$ with a hangdown hole in one end. The surfaces were glass-bead blasted to give uniform matte surfaces, and were cleaned ultrasonically in detergent, acetone, and ethanol.

Hot corrosion was induced by coating the samples with Na_2SO_4 prior to oxidation as described by Bornstein et al. (Ref. 3). Two doses were used: $2/3$ and 3 mg cm^{-2} .

Isothermal tests were performed at 900° and 1000° C in slowly flowing oxygen at one atmosphere pressure on both unoxidized

and preoxidized samples. The direction of flow of oxygen was downward and the speed was 20 cm min^{-1} . Continuous gravimetric measurements were made using a Cahn R-100 microbalance. Corrections in the weight change were made for the buoyancy effect. Exposure times extended in some cases to over 400 hours.

In the induction period studies, hot corrosion was induced with coatings of 3 mg cm^{-2} at 900°C using samples that had been preoxidized for 100 hours at 900°C . Samples were run for set periods of time, and, after cooling, were water washed, usually for 15 minutes in warm water. The resulting solutions were analyzed for $\text{SO}_4^{=}$ and metal cations and anions.

The morphology and composition of all oxide scales were examined by X-ray diffraction, light microscope, electron microprobe, SEM, and ESCA.

RESULTS AND DISCUSSION

Straight Oxidation Studies. The oxide scales formed on complex nickel-base superalloys are a complicated mixture of several individual oxides, the nature of which depends on many factors. However, for simplification, the alloys are often classified as "alumina formers" or "chromia formers." The alumina formers are characterized by a nonparabolic, nearly logarithmic₂ rate law with weight gains of the order of 0.2 to 0.5 mg cm^{-2} . The scale is composed of a thin, continuous layer of Al_2O_3 adjacent to the metal substrate. The chromia formers are characterized by a parabolic, or paralingar, rate law with weight gains of the order of 1 to 5 mg cm^{-2} after 100 hours at 900° or 1000°C . The scale is characterized by a predominant Cr_2O_3 layer, usually with a region of internal oxidation of aluminum just beneath.

Our studies have shown that, in oxygen, B-1900 and VIA are primarily alumina formers, while 713C and 738 are chromia formers. This is unusual for 713C as it behaves as an alumina former when oxidized in air (Ref. 4).

Comparative Hot Corrosion Studies. Hot corrosion runs were conducted for all four alloys at 900° and 1000°C with two doses of Na_2SO_4 : $2/3$ and 3 mg cm^{-2} . Both unoxidized and preoxidized

(100 hrs. at temperature) samples were studied.

In Figures 1 and 2, we present the results obtained at 900°C for the 2/3 and 3 mg cm⁻² doses, respectively. The reproducibility of the data was roughly ±15% for duplicate samples. The induction period is not so obvious in Figures 1 and 2 because of the relatively insensitive time scales. Nevertheless, the onset of hot corrosion in all four alloys was preceded by an induction period. The induction period was generally followed by a period of rapidly accelerating weight gain that either consumed the entire sample: catastrophic oxidation; or transformed into a period of decelerating weight gain resulting in final cessation of oxidation: enhanced oxidation. Generally, we found enhanced oxidation with the 2/3 mg cm⁻² dose and catastrophic oxidation with the 3 mg cm⁻² dose.

The order of decreasing susceptibility to hot corrosion shown in Figures 1 and 2 is: B-1900 > 713C > VIA > 738, and this order was generally the same for all our results regardless of dose of Na₂SO₄ or temperature. It should be noted that 713C, a chromia former under the conditions of our experiments, is slightly more susceptible to hot corrosion than is VIA, an alumina former. In fact, the order of decreasing susceptibility is not the order of increasing chromium content, but is the order of decreasing molybdenum content: B-1900, 3.6; 713C, 2.4; VIA, 1.3; 738, 1.0 (in atomic percent).

It is noteworthy that 738 appears to be hot corrosion resistant for a considerable time, but after 200 hours undergoes very rapid catastrophic oxidation for the 3 mg cm⁻² dose (Fig. 2). In effect, it appears to have a very long induction period.

Preoxidation of the samples for 100 hours at temperature before hot corrosion had the effect of increasing the induction period markedly at 900°C, but only slightly at 1000°C. For example, the induction period at 900°C for B-1900 was extended from 1/2 to 6 hrs. for the 2/3 mg cm⁻² dose, and from 2 1/2 to 7 1/2 hrs. for the 3 mg cm⁻² dose; for 738 at 900°C and 3 mg cm⁻² dose, the induction period was greater than 450 hrs., the length of the test. At 1000°C, the induction period is a much less important feature of the hot corrosion curve being only 10 to 15 minutes long.

It was found that though the induction period is increased by preoxidizing the samples, after the onset of hot corrosion, the rate of corrosion is the same as for nonpreoxidized samples; i.e., the hot corrosion curve is merely displaced in time and the extent of corrosion is the same for either type sample.

The oxide scales formed during hot corrosion usually peeled off upon cooling to room temperature. They were composed of all the oxides of the metals in the alloy, NiO, of course, being the most prevalent. One combination oxide, NiMoO_4 , was especially prominent in all four alloys, but especially in B-1900 and 713C. Interestingly, the oxide on VIA contained considerable $\text{Na}(\text{Ta}, \text{W})\text{O}_3$.

Induction Period Studies. Samples of B-1900 preoxidized at 900°C for 100 hrs. were subjected to hot corrosion at 900°C by coating with $3 \text{ mg cm}^{-2} \text{ Na}_2\text{SO}_4$. Runs were continued for set periods of time as depicted by the arrows on the hot corrosion curve shown in Figure 3. The induction period in these experiments was roughly four hours. The actual value for individual samples varied, but all samples were normalized to a four hour induction period by matching the weight gain with the curve depicted in Figure 3.

The analytical results of the water soluble elements and $\text{SO}_4^{=}$ obtained from washing the samples are presented in Figure 4. We have plotted the amount of each element in milligrams against the length of time the sample underwent hot corrosion. The amount of $\text{SO}_4^{=}$ and Na originally applied to the samples is given at zero time. The total Na_2SO_4 was: $3 \text{ mg cm}^{-2} \times 7 \text{ cm}^2 = 21 \text{ mg}$.

The sodium is completely recovered in all samples within the recovery ability of the simple water-washing process; some Na is imbedded in scale and is not dissolved. The $\text{SO}_4^{=}$ disappears rapidly, just at the end of the induction period. Soluble aluminum appears just after the induction period, indicating that the layer of Al_2O_3 on the alloy that protects it from oxidation has been dissolved. The soluble aluminum disappears for longer time periods indicating reformation of Al_2O_3 , but not as an intact layer. Soluble chromium, which was not included in Figure 4 for sake of clarity, behaves in a fashion similar to aluminum, but reaches measurable values earlier in the induction period attaining a maximum of 2.2 mg. On the other hand, soluble nickel (also not included in Figure 4) was not observed until after the aluminum had maximized. It attained a value of 2.5 mg which

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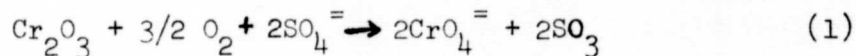
tailed off gradually to a value of 1 mg.

The most striking feature of the results is the large amount of soluble molybdenum that appears just at the end of the induction period and beyond. At first thought, one might not expect soluble molybdenum to exceed that required to tie up the available Na as Na_2MoO_4 . However, it must be remembered that MoO_3 is soluble in water to the extent of 2 g in 100 ml water at 70°C . This does not detract from the fact that considerable molybdenum has been oxidized in the early stages of the hot corrosion process.

Elemental X-ray micrographs of cross-sections of these hot-corroded samples were made. In Figure 5, we show the micrographs for several elements in the oxide scale of the $4\frac{1}{2}$ hr. sample; i.e., for a time just after the induction period, at the beginning of the period of rapidly accelerating oxidation. The protective Al_2O_3 layer has been dissolved and aluminum is dispersed throughout the oxide scale. The most unusual feature of these data is the position of the molybdenum concentrated along the oxide-alloy interface. This segregation is prominent in long time samples also and has been reported previously by Goebel, Pettit, and Goward (Ref. 1) and by Bourhis and St. John (Ref. 5).

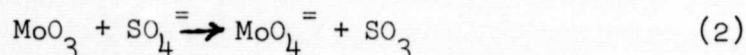
Mechanistic Implications. The segregation of molybdenum along the alloy-oxide interface observed in the samples undergoing hot corrosion coupled with the large quantity of molybdenum detected in our analysis indicate that B-1900 hot corrodes by an "acidic fluxing" mechanism (Ref. 1) in contrast to the "basic fluxing" mechanism (Ref. 6). The results of our Induction Period Studies can be explained by the following sequence of reactions.

Initially, the Cr_2O_3 on our preoxidized samples is oxidized to soluble $\text{CrO}_4^{=}$:



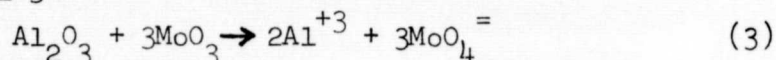
This reaction continues throughout the induction period and consumes at most a few milligrams of SO_4 .

Concomittantly, MoO_3 in the oxide is dissolving in the Na_2SO_4 , consuming it by the reaction



In addition, the quantity of MoO_3 increases rapidly due to further oxidation of molybdenum carbides³ lying in the surface oxide (Ref. 1).

By the end of the induction period, the MoO_3 has locally lowered the oxide ion activity in the melt to the point where dissolution of Al_2O_3 by "acidic fluxing" can take place:

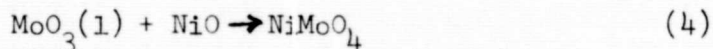


At this point, the molten phase can creep beneath the Al_2O_3 layer and spread over the sample as observed by Goebel, Pettit, and Goward (Ref. 1) and by Bourhis and St. John (Ref. 5).

The nature of the molten phase at this time is probably a mixture of MoO_3 (mp: 795°C) and Na_2MoO_4 (mp: 687°C). Our results indicate that little or no molten Na_2SO_4 is present in contrast to the hypothesis of Goebel, Pettit, and Goward (Ref. 1). It should be noted that the atomic weight of molybdenum is the same as the molecular weight of SO_4 . Therefore, there is sufficient oxidized molybdenum to consume all the sulfate by reaction (2): Figure 4. Actually, we were not removing all the oxidized molybdenum by our water washing technique (as evident by the molybdenum in the micrographs), so the amount of molybdenum available for reaction (2) was probably considerably more than the amount reported in Figure 4.

The self-sustaining feature of the hot corrosion reaction arises from the presence of the molten phase, $\text{MoO}_3(l) + \text{Na}_2\text{MoO}_4(l)$, beneath the oxide scale adjacent to the alloy surface. The oxidation propagates by a process similar to that described by Brenner (Ref. 7) for Fe-Cr-Mo and Fe-Ni-Mo alloys.

The self-sustaining feature may be compromised by the reaction:



This process replaces the liquid MoO_3 with a solid phase and accounts for the prominence of NiMoO_4 in all the hot corrosion scales. For the small dose of Na_2SO_4 ($2/3 \text{ mg cm}^{-2}$) used in this

study, oxidation ceased due to reaction (4). For the large dose (3 mg cm^{-2}), oxidation continued until the sample was consumed, probably because $\text{Na}_2\text{MoO}_4(1)$ formed a larger fraction of the molten phase, and removal of $\text{MoO}_3(1)$ by reaction (4) was not as critical as with the smaller dose.

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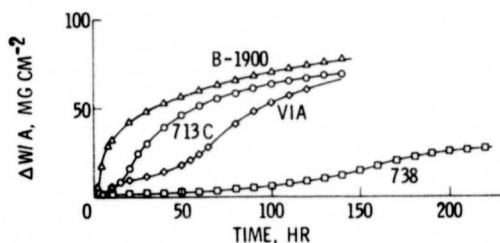


Fig. 1. - Comparative hot corrosion - 900°C, 2/3 mg cm⁻² Na₂SO₄.

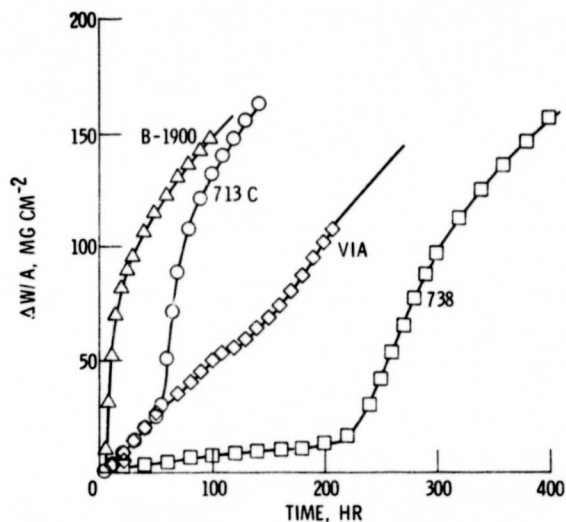


Fig. 2. - Comparative hot corrosion - 900°C, 3 mg cm⁻² Na₂SO₄.

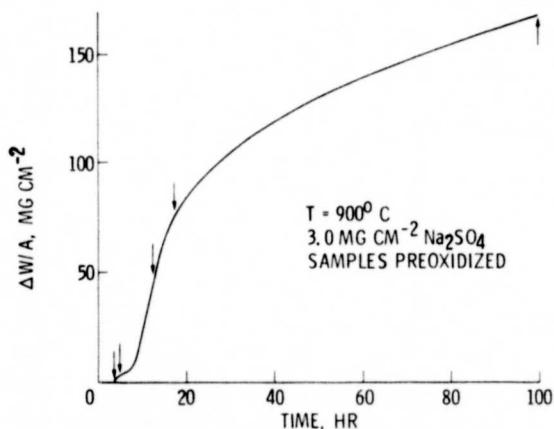


Fig. 3. - Typical hot corrosion curve for B-1900 preoxidized samples.

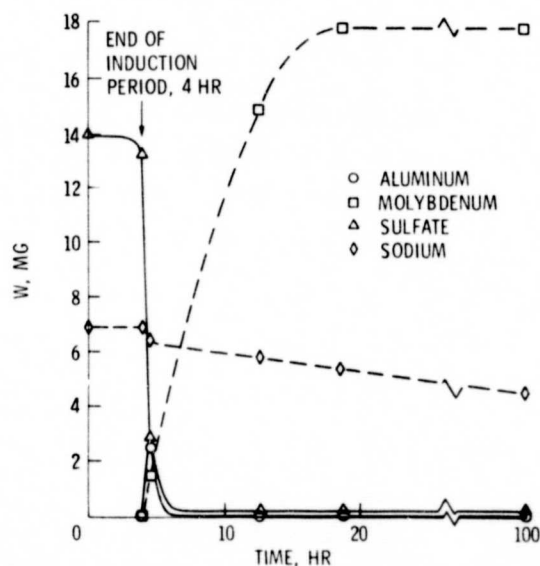
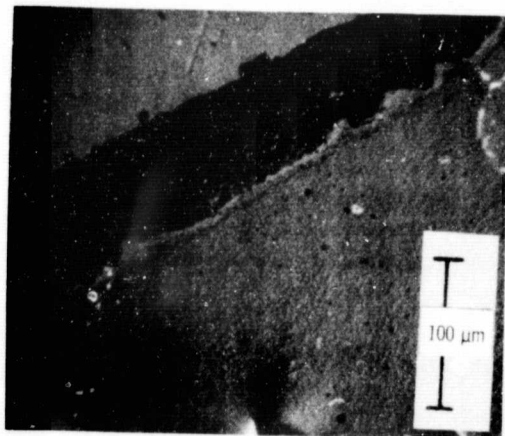
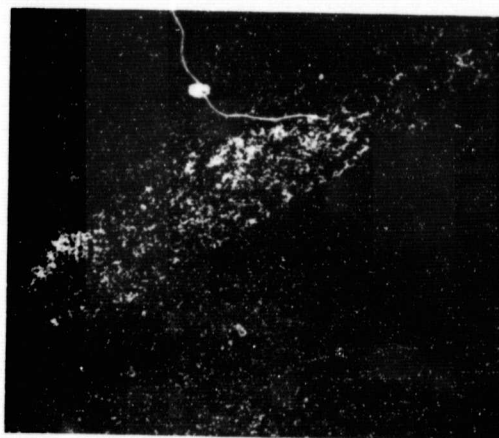


Fig. 4. - Water soluble elements found after various periods of hot corrosion - B-1900 preoxidized samples, 900°C, 3 mg cm⁻² Na₂SO₄.

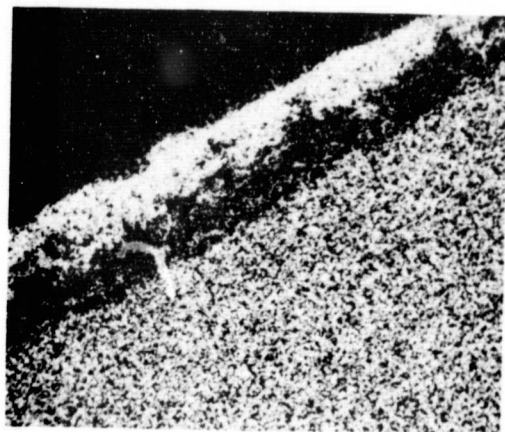
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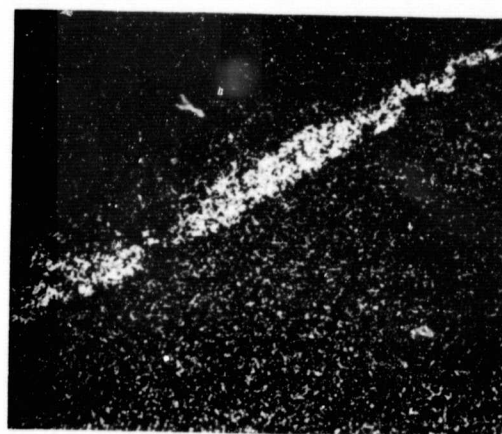
BACK-SCATTER ELECTRONS



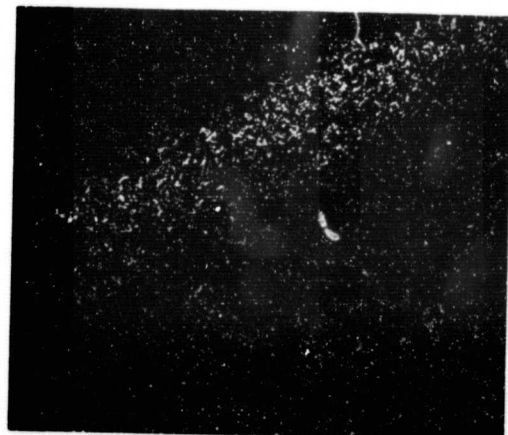
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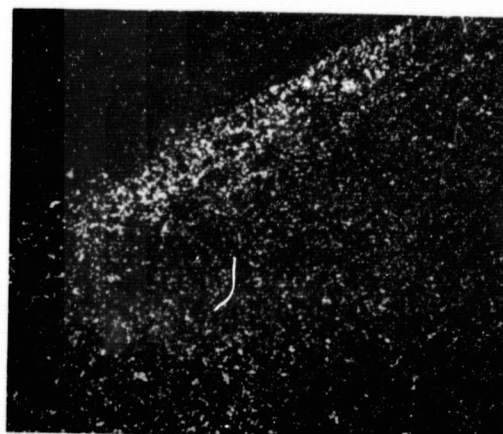
CHROMIUM



MOLYBDENUM



OXYGEN



ALUMINUM

Figure 5. - Back scattered electron and elemental x-ray micrographs of hot corroded sample - B-1900, preoxidized, 900° C, 3 mg cm⁻² Na₂SO₄, 4.5 hrs.